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Adsorption of atrazine on representative Massachusetts soils.

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ADSORPTION OF ATRAZINE
ON REPRESENTATIVE MASSACHUSETTS SOILS

By

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I. INTRODUCTION

Atrazine is a widely used selective and non-selective herbicide. It is applied to soils at rates of from 2 to 4 pounds per acre to control such annual weeds as morning glory, barnyardgrass, cheatgrass, giant foxtail, pigweed and wild lettuce (30, 62). Northern nutgrass and quackgrass are also controlled by atrazine (13, 109). Atrazine has been used to control these weeds in crops of corn, sorghum, sugar cane, macademic orchard, pineapple, grapes, asparagus, fruit trees, and turfgrass sods of several bentgrasses, fescues and perennial ryegrasses (33, 58). It is used in some areas for selective weed control in conifer reforestation, Christmas tree plantations and grass seed fields. Atrazine is also widely used as a non-selective herbicide to control vegetation in non-crop lands and in range land improvement (30). Depending upon the crop or intended use, atrazine may be used as a pre- or post-emergence herbicide, but the atrazine must be applied before weed seedlings are more than 1 1/2 inches high (49). Aerial application has been very successful, especially when wet weather or rough terrain makes ground application impractical (13, 41).

Plants absorb atrazine through both roots and foliage (58). The symptoms of the herbicidal effect of atrazine closely resemble those caused by monuron, a substituted urea herbicide. Both herbicides cause chlorosis and drying of the leaves and collapse of the stems and petiols (20, 89).

Chemical weed control is one of the most important recent advances in agriculture and atrazine is one of the most widely used herbicides for soil application.

Atrazine has high phytotoxicity and also has considerable residual toxicity in the soil. Enough atrazine has been shown to remain in the soil six months to two years after application to bring about marked toxicity for oats (15, 16, 98, 110).

The resistance of this herbicide to breakdown in the soil has caused some problems. One of these comes from the practice of crop rotation (15, 115). Some crops are resistant to the herbicidal effect of atrazine while others are not. Thus, crops sensitive to injury by atrazine such as oats, soybeans, tobacco, sugar beets and many vegetable crops may be injured if they are planted in a field where atrazine has been used to control weeds (20, 30, 94). Several processes may be involved in determining the fate of atrazine applied to the soil, including absorption by plants, photodecomposition (55), volatilization (56), breakdown by micro-organisms (68, 101), and adsorption by the soil. Herbicides adsorbed on soil particles may be transported by flowing water from the point of application to streams, rivers, and to lakes. Leaching of atrazine from the surface soil to a depth lower in the soil profile may result in greatly reduced breakdown because of lower soil temperature and microbial activity. The ultimate fate of the herbicide leached from the surface soil may be to contaminate ground water. Thus, application of herbicides may lead to water polution. It is necessary to investigate the behavior of atrazine in soils in order not only to use it most efficiently but also to evaluate the possibility of water polution as a result of application of this herbicide (14).

Adsorption of atrazine by soil particle will have great influence on the fate of this compound after it is applied to soils. Atrazine is widely used in Massachusetts

as well as in other states. No study has been conducted up to this date on the interaction between this herbicide and soil of Massachusetts. This study of atrazine adsorption by soils from Massachusetts may provide some useful information directly for atrazine and generally for other herbicide behavior in Massachusetts.

II. LITERATURE REVIEW

Atrazine, 2-chloro-4-ethylamino-6-isopropylamino-s-triazine, has the empirical formula $C_8H_{14}ClN_5$ and a molecular weight of 215 (69). The chemical structure of this molecule is shown in Figure 1.

Atrazine is sparingly soluble in water. A saturated solution contains 22 mg/l at 0°C and 70 mg/l at 27°C. It is a very weak base with pK value in water at 22°C of 1.68. As indicated by the pK value of atrazine, in the range of soil pH of 4 to 9 normally found in nature, the predominant form of atrazine is the neutral molecule. At pH 1.68, 50% of the atrazine would be present in solution as the cation, but at pH 4, less than 2% would be in cationic form at 22°C (59).

Atrazine is stable in neutral, slightly acidic or basic media but it is hydrolyzed to the herbicidally inactive 2-hydroxy-4-ethylamino-6-isopropylamino-s-triazine in acidic or basic media, especially at higher temperatures (59). This hydrolysis of atrazine has been found to be one of the detoxification processes in resistant plants (17, 73, 74, 78) along with dealkylation of the molecule to 2-chloro-4-amino-6-isopropylamino-s-triazine (42, 92, 93).

Atrazine added to soils may be adsorbed on both clay and organic colloidal particles. Although there have been few studies of the mechanism of adsorption of atrazine and similar compounds on soil organic matter, there have been several studies of these compounds on clay minerals. Among the mechanisms that have been proposed to account for adsorption of these compounds on clay minerals are

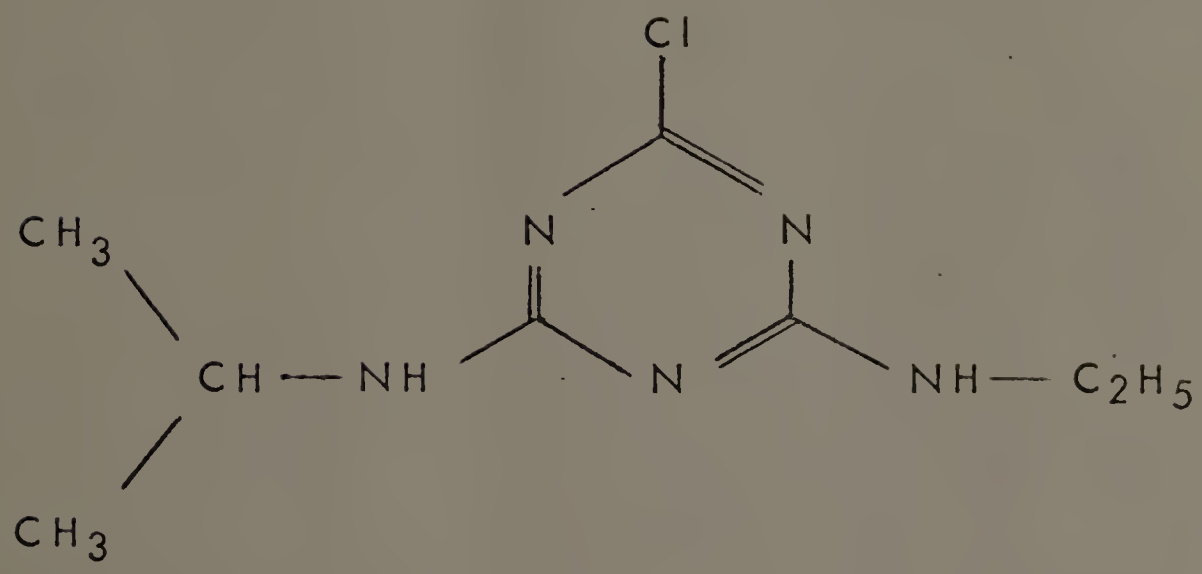

Figure 1. Chemical structure of atrazine

van der Waals' bonding, cation exchange and H-bonding.

Most of atrazine is present as the neutral molecule under normal soil conditions. Similar non-polar molecules such as pyridine and various C-substituted aliphatic derivatives of pyridine molecules were found to form only van der Waals' bonds with montmorillonite and halloysite, where alkyl residues of the organic molecules all lay as flat as possible between the mineral sheets as shown by X-ray diffraction studies (32, 35, 36, 46, 65, 67). The orientation of the molecules between the silicate sheets was found only to occur in restricted ways. It was concluded that many molecules reoriented at higher surface concentrations so as to facilitate a closer packing of molecules on the surface of the adsorbing particles (31, 103). The adsorption of these neutral molecules on the clay surface was closely related to the total surface area of the clay (4, 21). At the pH range of 5 to 7, no adsorption of atrazine and simazine by kaolinite was detected. Illite and montmorillonite were similar in their capacity to adsorb these compounds, although montmorillonite had a cation exchange capacity four times as large as illite. It was concluded that perhaps the triazine herbicides were unable to penetrate into the internal surfaces of the expanding lattice type montmorillonite clay (21). The magnitude of van der Waals' forces are directly related to molecular weight which was closely related with molecular size. In general, the van der Waals' forces were so weak that these organic molecules were displaced from the clay surface by water molecules (9, 19, 25, 39, 75). It was concluded that the formation of clay-organic complex did not proceed

through random adsorption, but that once a few molecules were adsorbed as nuclei succeeding molecules were adsorbed in a manner similar to a crystallization (7, 8, 9, 19, 53, 104).

Van der Waals' bonding is not pH-dependent. But, it has been observed that lowering the pH of the adsorption system increased the amount of atrazine, simazine, related triazine compounds and other similar herbicides adsorbed on clay minerals (18, 28, 43, 45, 76, 90, 102). The pH effect on the adsorption reaction implies that there is an adsorption mechanism in addition to van der Waals' bonding. A mechanism that would be pH-dependent is cation exchange (2, 12, 36, 37). Lowering pH would increase the proportion of cations of these weak bases in solution.

Another possible mechanism for atrazine adsorption is H-bonding to so-called free silanol groups on the clay surface (29, 95). Adsorption of atrazine and other s-triazine herbicides by montmorillonite clay was attributed to van der Waals' bonding at higher pH values and a combination of cation exchange forces and direct association with H ion on the clay surface at low pH values (111). The adsorption was observed to increase rapidly at a pH in the vicinity of the pK value of each compound (111). For atrazine, the pK is below 2. Such acid soil conditions do not exist in the field.

Very few studies on the adsorption of atrazine and related organic compounds by soil organic matter have been reported. The adsorption of atrazine and simazine by a humic acid was found not to be reversible by the overwhelming number of highly polar water molecules (11, 25, 39, 70, 71). Soil organic matter has been given

Increasing attention as the most important factor responsible for the adsorption of organic compounds applied to the soil (1, 5, 10, 24, 44, 47, 48, 50, 61, 81, 84, 88, 91, 106, 107, 108, 112). Identification of individual compounds of soil organic matter has been attempted but the elimination of chemical modification during the process has not been possible (40, 66, 72, 96, 97, 114, 116). Whether or not a unit amount of soil organic matter from different soils has similar adsorption power is unknown (57, 85). It is very unfortunate that the properties and nature of soil organic matter are not revealed enough to explain clearly the role of it in the adsorption reaction where it has been suggested as the most active of all the soil constituents.

The pressure of soil organic matter seemed to deprive the clay of taking a role in the adsorption process of organic compounds in the soil (63). It was reported that the electrical properties of the clay and organic colloids were modified when complex formation occurred. There was generally a marked reduction in the electronegative charge of the two colloids (22). The complex formation of soil organic matter with clays and metal ions present in the soil (82, 83, 86, 87), coupling with the fact that the organic-organic interaction is stronger than organic-inorganic interaction, seems to be the factor which influences the adsorption power of clay minerals. Perhaps where the clay surface is occupied by soil organic matter before addition of an herbicide, adsorption of the herbicide by clay is prevented. Many have postulated that soil particles are held together in aggregates by organic compounds present in the soil (34, 38, 51, 60, 69, 99, 100).

Since adsorption is an exothermic process, adsorption might be expected to decrease with increasing temperature (43, 70, 102, 113). Adsorption of atrazine and simazine by *Marshall* silty clay loam decreased with increasing temperature (102). On the other hand, it was observed that the adsorption of atrazine on a humic acid increased with increasing temperature (70). The lack of temperature dependence of adsorption of organic compounds in organic soils has been observed in several herbicide studies (43, 105). This phenomenon may tell the degree of the interaction between the clay colloids and organic colloids in the adsorption reaction of organic compounds in the soil.

The relationship between the residual toxicity of simazine and some properties of soils of Arizona and California showed in simple correlation analyses that the residual toxicity in the soils was positively correlated with soil organic matter and cation exchange capacity, and negatively correlated with pH. Multiple regression analyses suggested that the negative correlation between the simazine residual toxicity and pH was a consequence of the correlation between organic matter and pH (90). Adsorption of atrazine by Missouri soils was generally associated with organic matter content, clay content, cation exchange capacity and exchangeable magnesium and hydrogen. The relationship between adsorption of triazines and organic matter and clay content were expected because of the colloidal nature of these constituents. However, the organic matter was generally much more adsorptive than the clay (102). A study of the adsorption of simazine by soils of the Southeast showed that the adsorption of this herbicide was not correlated significantly with

per cent clay but was correlated highly significantly with organic matter and titratable acidity (76).

Saturation of a soil to various levels of base saturation by different cation species was found to affect atrazine and simazine adsorption primarily by the influence of the accompanying hydroxide ion on the hydrogen ion activity of the soil system. Adding salts such as $Ca(OH)_2$, NaOH and KOH resulted in decrease in adsorption of atrazine in Bayboro clay soil. It was also observed that triazine adsorption sites were proportional to the titratable acidity of the soil. The decrease in adsorption of these compounds appeared to be a result of the occupation of adsorption sites by the cation, rather than a specific effect of cation species on the adsorption of these herbicides (77). Adding aluminum sulfate to the soil reduced injury from simazine on pine seedlings, perhaps because lowering of the pH of the soil increased adsorption of the herbicide (23). Many have reported, however, that adsorption is nearly independent of pH in the presence of organic matter in soils (27, 54, 76, 90).

III. MATERIALS AND METHODS

Samples of 14 surface soils and 6 soil profiles were collected from different locations in Massachusetts. The surface soil samples are described in Table I in the Appendix (6), and the soil profiles are described in Table II in the Appendix (6). They were passed through a 2-mm screen and thoroughly mixed. To determine the amount of exchangeable Ca, Mg and K, the sample was extracted with 1 N ammonium acetate and the amount of each cation was measured using a Perkin Elmer Model 214 Atomic Absorption Spectrophotometer. To determine the exchangeable Al content, the soil was extracted with 1 N KCl and the amount of Al was measured by aluminon method described by Jackson (52). Total exchangeable hydrogen and aluminum content was determined by extracting the soil with 1 N KCl and titrating the extract with 0.02 N NaOH. Organic carbon content of the soil samples was determined using the Walkely-Black method (3). It was very difficult to dissolve atrazine in water because of the slight solubility of atrazine. However, the fairly high melting point, increasing solubility at higher temperature and non-volatile property allowed the following procedure to be used to prepare atrazine solutions. One-hundred mg of purified 99.2% atrazine was dissolved in 100 to 150 ml of ethanol. The solution then was transferred into a 2000 ml volumetric flask and about 80 ml of warm water was added. The flask was then placed in a boiling water bath to evaporate ethanol from the solution. The evaporation of ethanol from this solution could be observed. After completing evaporation, an amount of warm water was added to make the volume

2000 ml, then time was allowed for the solution to cool to room temperature. The volume of the solution was then made 2000 ml by adding water. This process provided a 50 ppm stock solution which was diluted as required for the experiments. The solution used for each soil sample contained 0.01 M $CaCl_2$ to simulate the salt concentration in the soil solution in the field. The concentration of atrazine solution was about 2 ppm except in the experiments in which the atrazine concentration or the soil to solution ratio was varied. In the former experiment the concentration was varied from 1 ppm to 20 ppm and in the latter it was 20 ppm.

In order to measure atrazine adsorption, a weighed soil sample was placed in a 250 ml Erlenmeyer flask, atrazine solution was added and then the flask was stoppered. The ratio of solution to soil was 2:1 except in the experiment of soil to solution ratio. The solution was not allowed to contact the stopper in order to prevent adsorption of atrazine by the stopper. The soil sample was equilibrated with the atrazine solution for 24 hours on a mechanical shaker at a temperature of about 24°C. After equilibration the solution was filtered through Whatman No. 42 filter paper to obtain the clear supernatant solution to be used for analysis. Upon filtering, the pH of the soil extract was observed to decrease, perhaps due to ion exchange between Ca ion in the soil solution and H ion retained originally on the filter paper. However, no adsorption of atrazine by the filter paper was detected.

Adsorption of atrazine was determined by measuring the change in concen-

tration of the aqueous solution upon contact with soil sample. The difference in concentration was assumed to be due entirely to adsorption.

Two different methods of analysis were employed. In the experiments of time and equilibrium of adsorption, salt concentration and adsorption, equilibrium solution concentration and adsorption, adsorption by 14 surface soils and adsorption by soil profiles, atrazine concentration were measured using the method described by Knusli (59).

The sample to be tested was extracted with 50 ml of CH_3Cl in a 125 ml separatory funnel. The CH_3Cl extract was then washed twice with 50 ml of 2% NaOH, three times with 50 ml of 0.5 N HCl, and finally once with 50 ml of water. Afterward the washed extract was rinsed into a clean 50 ml beaker. Small drops of water suspended in the CH_3Cl would cause a slight turbidity and were removed by filtering through cotton wool. The extract was concentrated to a volume of about 10 ml to 15 ml on an electric hot plate and transferred into a clean 125 ml separatory funnel. The beaker was rinsed with a small amount of CCl_4 and the rinse was added to the extract in the separatory funnel. The final volume was between 20 and 25 ml. One ml of 50% H_2SO_4 was added, shaken for 30 seconds and allowed to stand for at least 30 minutes. This procedure was repeated three times. At the end of the fourth 30-minute period, the hydrolysis was completed and 9 ml of water was added and mixed gently. After separation of the layers, the bottom layer was drawn off and discarded. The upper aqueous layer was washed once with 50 ml of CH_3Cl. The washed aqueous layer was poured

into another clean 125 ml separatory funnel and shaken with 25 ml of diethylether to remove CH_3Cl which would interfere with determination at 225 millimicrons. An aliquot of the aqueous layer was transferred directly into a 1-cm quartz cell for reading. In as much as silica would interfere with the reading, stopcock grease was not used. The absorbance was measured at 225, 240 and 255 millimicrons using a Carl Zeiss Spectrophotometer PMQ II with a hydrogen lamp. To determine the atrazine content, it was necessary to prepare a calibration curve using known amounts of atrazine. The measured absorbance gave the difference, Δ , by the following equation:

$$\Delta = A^{240} - \left(\frac{A^{225} + A^{255}}{2}\right)$$

where A^{λ} was absorbance at wavelength λ. The difference was corrected by subtracting a blank value obtained for the reagents used. Throughout the experimental period redistilled water was used to eliminate the interference of organic substance present in the ordinary distilled water which was available in the laboratory.

In the experiment of soil to solution ratio, the pyridine-alkali method (59, 79) was used to measure atrazine concentration. The method was modified from that which was described in the original reference (79). This modification was required partly because of the present laboratory apparatus and partly because of the experimental difficulty that would come from the color interference by soil organic matter. The filtered extract was then diluted ten-fold with distilled water for analysis. The concentration of atrazine was determined by taking the

difference between apparent atrazine concentration of the soil extract and the apparent concentration of another soil extract prepared at the same time but without added atrazine. Eight ml of the diluted extract was pipetted into a graduated test tube. Then, 2 ml of 70% pyridine was added and mixed. Afterward 2 ml of 0.25 M citric acid buffer (pH = 4) was added and mixed thoroughly. The tube was then placed in a boiling water bath for 30 minutes and then cooled to 20°C in a water bath. A large glass marble placed on the tube served as a condenser to prevent excessive evaporation. After allowing time for temperature equilibration at 20°C, 2 ml of 9 N NaOH was added and the solution was mixed. Distilled water was added to the tube to make the total volume 15 ml. An aliquot of the solution was transferred into a 5-cm glass cell and the absorbance of the yellow solution was measured at 436.5 millimicrons, 1 minute after addition of NaOH. This was the time required for maximum color intensity to develop. The instrument employed was the Carl Zeiss Spectrophotometer PMQ II with an incandescent lamp. To determine the atrazine content it was necessary to prepare a calibration curve using a known amount of atrazine.

IV. RESULTS AND DISCUSSION

Review of Theory

When atrazine is added to a moist soil a chemical equilibrium will be established between atrazine in solution and atrazine adsorbed by the soil. The simplest chemical equation representing this equilibrium is:

$$\text{(Atrazine)} + \text{Soil} = \text{Soil(Atrazine)} \qquad (1)$$

Assuming that equation (I) represents this reaction, the equilibrium constant Keq may be written as:

$$K_{eq} = \frac{[\text{Soil(Atrazine)}]}{[\text{Solution(Atrazine)}]\ [\text{Soil}]} \qquad (2)$$

When the amount of atrazine is small in comparison to the capacity of the soil to adsorb atrazine, the "[Soil]" term in equation (2) will remain practically constant. Under conditions where this condition is fulfilled, the "[Soil]" term in equation (2) may be eliminated and the equilibrium should be represented by equation (3):

$$K_{eq'} = \frac{[\text{Soil(Atrazine)}]}{[\text{Solution(Atrazine)}]} = \frac{\text{(Atrazine)adsorbed}}{\text{(Atrazine)solution}} \qquad (3)$$

In order that this expression describe the equilibrium between atrazine in solution and that adsorbed on a particular soil as soil conditions are changed, certain conditions must be fulfilled; (I) organic molecules present in the soil either must not compete with atrazine for adsorption sites, or must be present in constant concentration as

soil conditions such as salt concentration or soil moisture content vary, (2) pH of the soil system must not change so as to alter the proportion of neutral and charged atrazine molecules in solution, and (3) the capacity of the soil to adsorb atrazine must not be changed as might occur if, for example, the stability of soil aggregates were altered either by varying the salt concentration or soil moisture content or if there were a large change in pH.

Another expression commonly used to describe adsorption of herbicides by soils is the distribution coefficient. The distribution coefficient (K_d) is defined as the ratio of the amount of atrazine adsorbed per unit weight of soil to the concentration of atrazine in solution. In this thesis, the amount of atrazine adsorbed is expressed as mg/kg of soil and the atrazine concentration is expressed as mg/l. The distribution coefficient may be represented by equation (4):

$$K_d = \frac{(\text{Atrazine})\text{adsorbed}}{(\text{Atrazine})\text{solution}} \qquad (4)$$

If Kd is measured at equilibrium, a comparison of equations, (3) and (4), shows that K_d is equal to Keq'. Thus, Keq' is a special case of K_d in this system. The K_d was calculated using equation (5):

$$K_d = \frac{(Ct - Ceq)}{Ceq} \cdot \frac{(V)}{(M)} \qquad (5)$$

where Ct and Ceq are the total concentration of atrazine added initially and the concentration of equilibrium solution, respectively. V represents solution volume

expressed in ml, and M represents the soil weight expressed in gm.

If adsorption of atrazine by soil follows an ordinary adsorption process, an empirical Freundlich equation may be used to describe the adsorption isotherm:

$$x/m = K\ C^{1/n} \tag{6}$$

where x and m are the amount of atrazine adsorbed by the soil and the unit weight of the soil, respectively. C is equilibrium solution concentration. K and n are empirical constants. Equations, (4) and (6), are equivalent if n is equal to 1 and then K is equal to K_d. Therefore, at equilibrium all three constants, Keq', K_d and K may be the same. This means that these constants may not change with changing atrazine concentration in the solution or the soil to solution ratio. To check the latter, equation (7) is derived from equation (5):

$$Ct/Ceq = Kd \cdot \frac{(M)}{(V)} + 1 \tag{7}$$

Thus, a graph of Ct/Ceq against (M)/(V) should have a slope equal to K_d and an intercept of 1, if K_d does not vary as the soil to solution ratio varies.

The purpose of the experiments conducted for this thesis is to determine the factors which are responsible for the adsorption of atrazine in soils from Massachusetts, and to determine whether the K_d for atrazine adsorption by a soil changes when the concentration of atrazine in solution changes or when the ratio of soil to solution changes.

Results and Discussion

A preliminary experiment was conducted to determine the amount of time required to attain equilibrium between atrazine in solution and atrazine adsorbed on the soil No. 3 and soil No. 9. The results are presented in Figure 2. The data show that maximum adsorption was attained within a few hours in agreement with other studies of atrazine adsorption by soils (77, 90, 102). The amount adsorbed after 3 hours was about 94% of that adsorbed after 24 hours of equilibration.

Most studies of atrazine adsorption by soils indicate that equilibrium is attained within a few hours. Nearpass (77) reported that Bayboro clay soil adsorbed about 97% as much as atrazine in a half hour as the soil adsorbed when equilibriated overnight. Talbert and Fletchall (102) reported that maximum atrazine adsorption by Missouri soils occurred within 1 hour. The results obtained with Massachusetts soils, No. 3 and No. 9, indicated that at least 3 hours were required for equilibration.

An experiment was conducted to determine what effect changing salt concentration in solution might have on atrazine adsorption by Soil No. 9. The results are presented in Table 1. The data show that salt concentration did not affect the amount of atrazine adsorbed in the range of normal salt concentration which may be expected in the soil solution and natural water. Varying concentration of $CaCl_2$ from 0.001 M to 0.1 M had no significant effect on the amount of atrazine adsorbed. However, at the concentration of 0.5 M $CaCl_2$ the amount

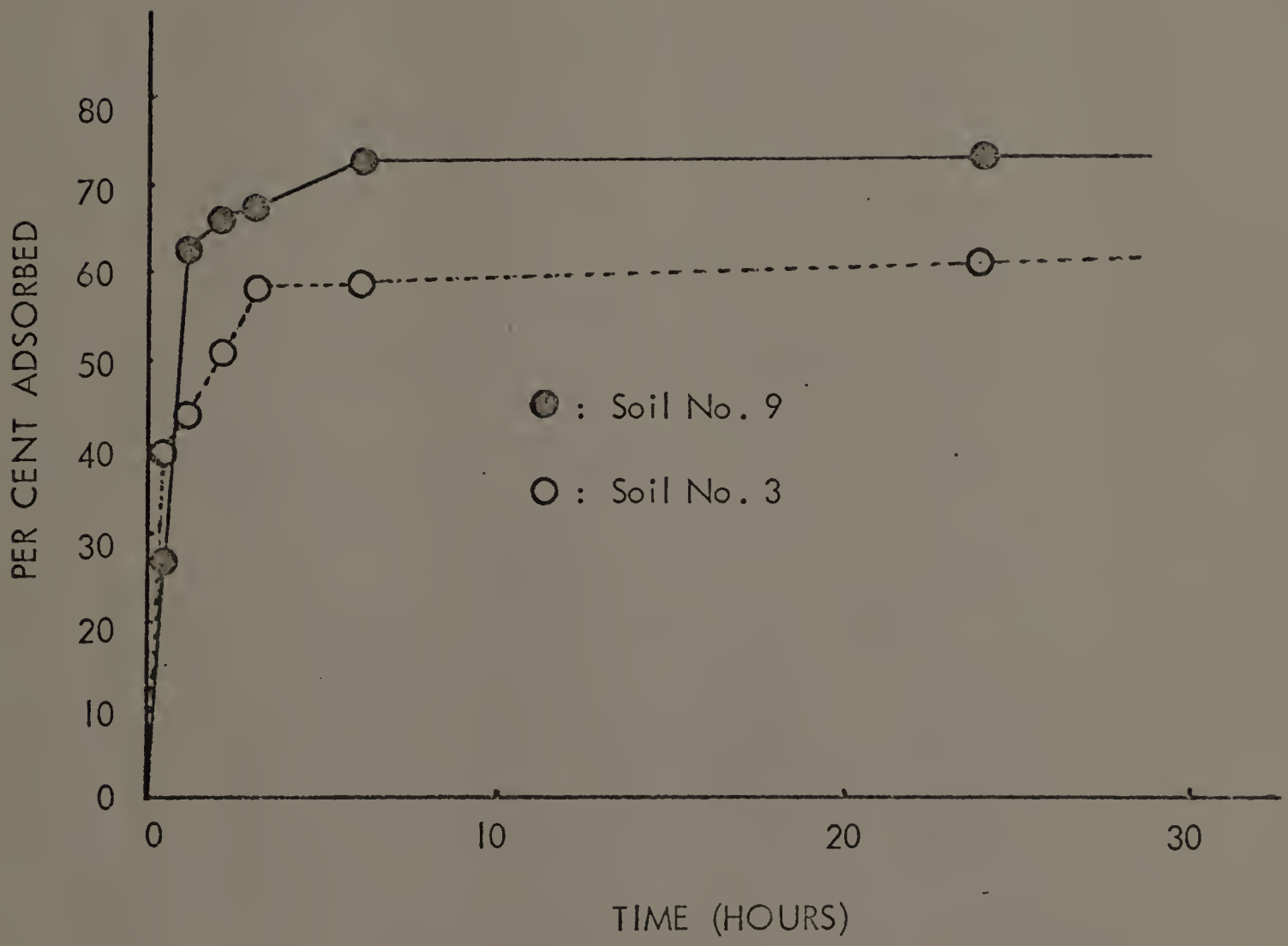

Figure 2. Effect of time on the per cent adsorption of atrazine by soil No. 3 and No. 9.

TABLE I

EFFECT OF SALT ($CaCl_2$) CONCENTRATION ON THE ADSORPTION OF ATRAZINE BY SOIL No. 9

Concentration of $CaCl_2$ (M)	Per cent Adsorption	K_d
0.001	49.7	1.98
0.005	47.2	1.80
0.01	50.0	2.00
0.05	46.7	1.75
0.1	48.6	2.80

of atrazine adsorbed increased. This increase in adsorption may be caused by a salting out effect, where the electrolyte added into an aqueous solution makes the solubility of a non-electrolyte smaller. The apparent increase in adsorption may be, in reality, a decrease in solubility.

In order to study the effect of soil properties on the atrazine adsorption the K_d for atrazine adsorption by 14 surface soils of Massachusetts were determined. The correlation coefficient (r) value showed that there was very close correlation between organic carbon content of the soil and K_d. The computed r was 0.73. An r value of 0.48 was required for significance at the 1% level. The regression line is $K_d = 1.42\%\ O\text{-}C + 0.05$. The regression line indicates that for an increase of 1% in organic carbon content, the K_d value increased 1.42. Soil No. 16 adsorbed much less atrazine than would be expected from the organic carbon content of the soil. Soil No. 12 had an abnormally high K_d value. When these two soils were excluded from statistical analysis, the regression coefficient was found to be 1.35.

Talbert and Fletchall (102) studied the adsorption of atrazine by Missouri soils. After converting the values of soil organic matter content they reported into the soil organic carbon content using the conventional factor of 1.724, the regression coefficient between the K_d and the organic carbon content was computed to be 2.00 for the Missouri soils. The value of intercept was 0.05. Comparison of the two regression coefficients, one of Massachusetts soils and the other of Missouri soils, revealed the difference in adsorption power, or probably adsorption

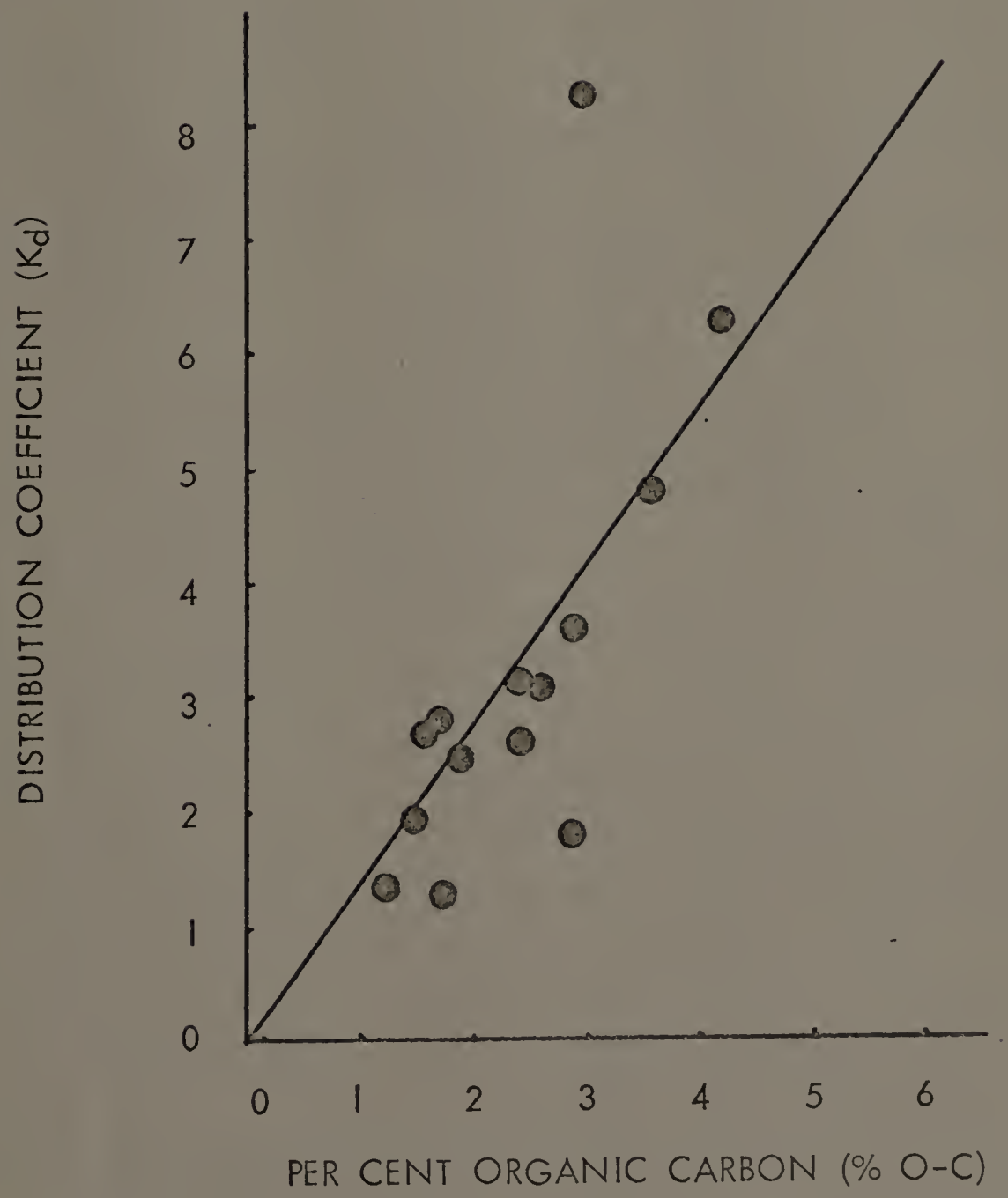

Figure 5. Relation of soil organic carbon content to K_d of atrazine of fourteen surface soils of Massachusetts.

capacity. The average value of K_d of Massachusetts soils was about 71% of that of Missouri soils.

The close correlationship between soil organic carbon contant and adsorption of atrazine was confirmed by results of measurement of atrazine by samples from different horizons of several soils. Typical results are presented in Figure 6. The data of this experiment is shown in Table II in the Appendix. Paxton fine sandy loam showed results reverse from the general trend. The reverse pattern of adsorption behavior of Paxton fine sandy loam should have been checked by experiments. Some useful suggestions may be drawn out from the general relationship between K_d and soil horizons in order to measure leaching of this herbicide, i.e., whether a certain amount of atrazine applied to the soil reaches the ground water level. Erickson (26) reported that as the adsorption capacity of the surface horizon or plowed layer became saturated, the excess of monuron moved downward through the soil profile.

The simple correlation analyses for the K_d value and some soil properties of Massachusetts soils are presented in Table 2, using the data of Table I in the Appendix. Soil No. 16, which has a very high clay content, showed very unusual properties compared with the other soils. In the analyses this soil was excluded. The K_d for atrazine adsorption on Massachusetts soils was correlated with clay content and very highly correlated with soil organic carbon content. The soil organic carbon content was highly correlated with the clay content. The K_d was not correlated significantly with the pH. This is in good agreement with the studies

TABLE 2

CORRELATION COEFFICIENTS (r) AMONG SOIL PROPERTIES AND K_d VALUE USING THE EXPERIMENTAL DATA FROM 13 SURFACE SOILS FROM MASSACHUSETTS*

	H + Al	% Clay	% O-C	K_d
pH	- 0.95	- 0.40	- 0.27	- 0.14
H + Al		0.28	0.11	- 0.02
% Clay			0.44	0.35
% O-C				0.79

*Correlation coefficient of 0.5 at 1% level and 0.4 at 5% level required for significance

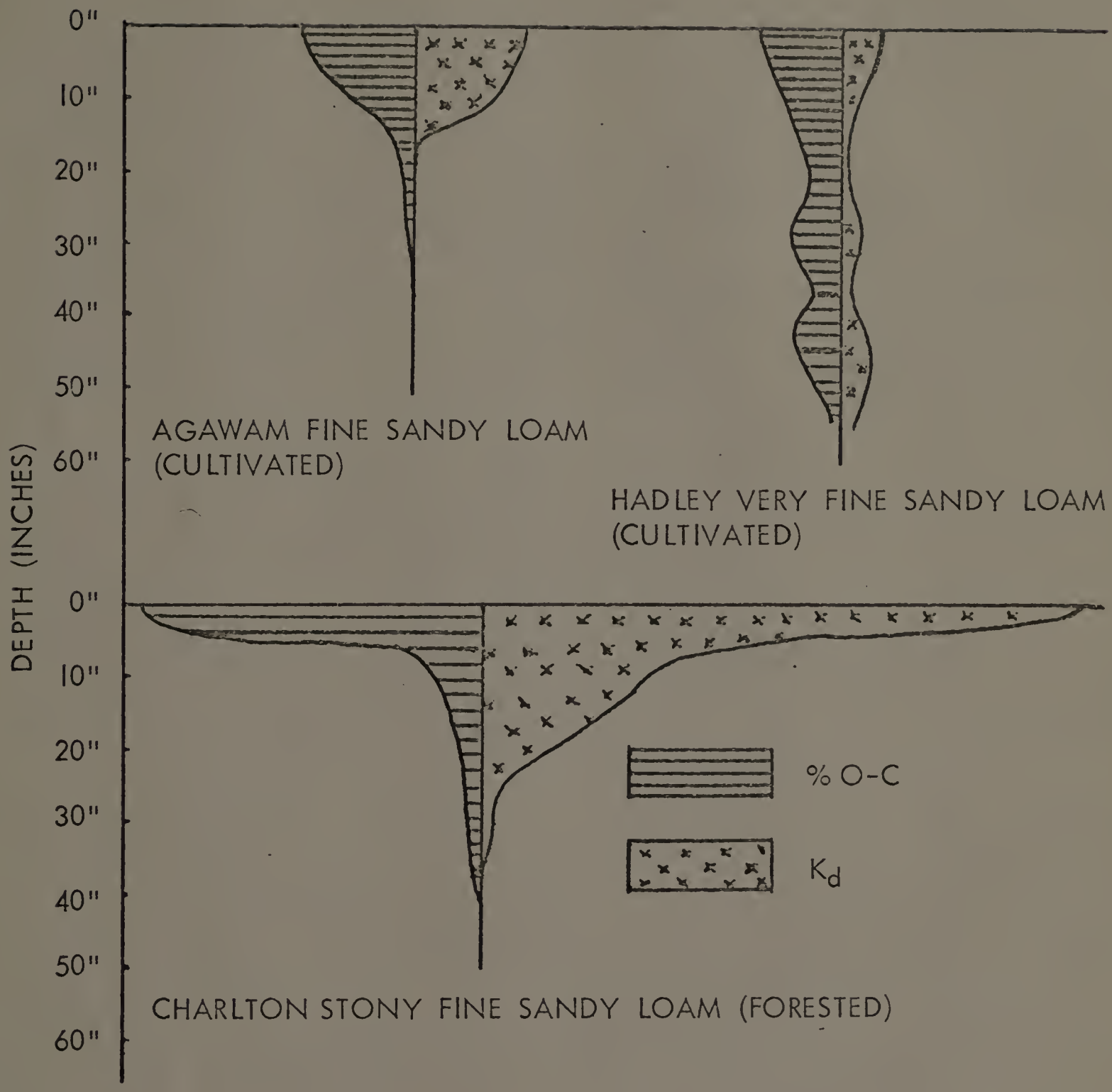

Figure 6. Relation of soil organic carbon content to the K_d of atrazine of soil profiles.

on the adsorption of atrazine by soils of Arizona and California (90), of Missouri (102), and of Southeastern section of the United States (76).

Two experiments were performed to determine whether or not the equilibrium between atrazine in solution and that adsorbed by soils could be described by equation (3). The results of measurement of the amount of atrazine adsorbed at equilibrium with several concentrations of atrazine are presented in Figure 3. The data can clearly be described by a straight line up to a concentration of at least 5 mg of atrazine per liter of solution. The average K_d value calculated from the points obtained is 2.02.

Consideration of the Freundlich equation shows that K is constant if the plot of log C against log x/m yields a straight line;

$$\log x/m = 1/n \log C + \log K \qquad (8)$$

If $n = 1$, then $K = K_d$ for the soil system under study. The plot of soil No. 9 showed a good straight line with log K value of 0.34. Thus, K is 2.2. This value is in good agreement with the average value of 2.02 obtained from the adsorption isotherm directly. The value of n is then 1.1. This is also a reasonable deviation from the theoretical value of 1. The results obtained here makes it possible to say that K_d of atrazine in soil No. 9 is constant, independent of the solution concentration.

A second experiment was designed to test equation (3) and to study the effect of changing the soil to solution ratio on the value of K_d.

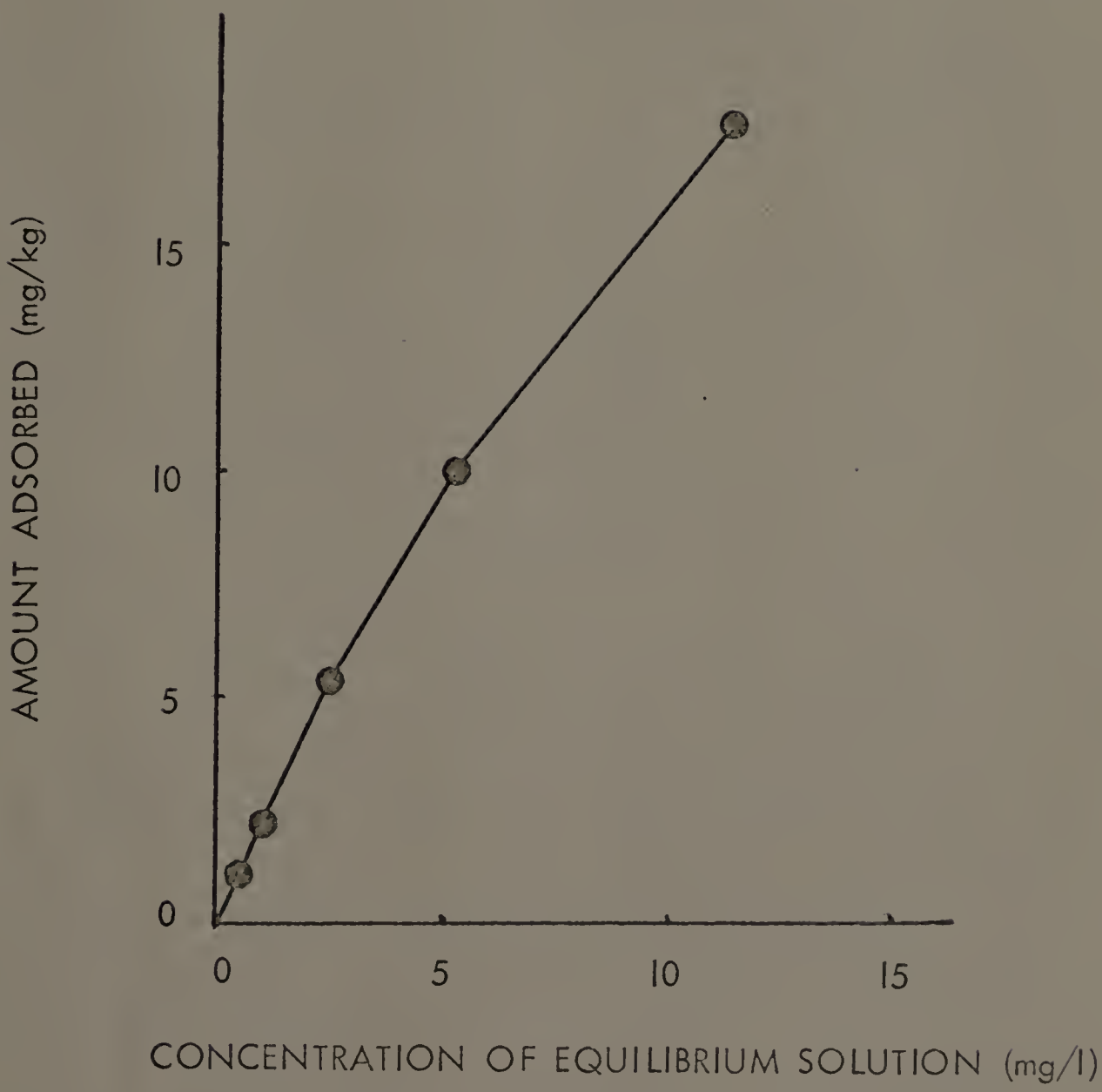

Figure 3. Isotherm for the adsorption of atrazine by soil No. 9.

It was presumed that the concentration of 20 ppm of atrazine solution was below the critical equilibrium solution concentration for all the samples taken for the experiment of soil to solution ratio. Equation (7) derived from equation (5) requires that if K_d is independent of soil moisture content the plot of (M)/(V) against the Ct/Ceq should yield a straight line with the slope equal to K_d. The amount of atrazine adsorbed by soil samples as the soil to solution ratio was varied from 0.1 to 1.0 was measured. The plots of the results are presented in Figure 4. The regression lines calculated to be:

$Ct/Ceq = 5.18\ (M)/(V) + 0.78$ (Soil No. 6) ($r = 0.999$)

$Ct/Ceq = 1.63\ (M)/(V) + 0.98$ (Soil No. 2) ($r = 0.999$)

$Ct/Ceq = 1.81\ (M)/(V) + 0.94$ (Soil No. 9) ($r = 0.999$)

$Ct/Ceq = 1.10\ (M)/(V) + 0.97$ (Soil No. 3) ($r = 0.997$)

Linear regression correlation coefficients (r) were calculated for each set of line. For soil No. 6 and soil No. 2, the r was 0.999. For soil No. 9 and soil No. 3, the r was 0.999 and 0.997, respectively. Widening the soil to solution ratio resulted in increase in adsorption of atrazine per a unit weight of soil sample. The linear regression correlation coefficients were high enough to state that all the experimental points were actually on the regression line. Therefore, K_d is strictly constant within the range of the ratio studied. Only

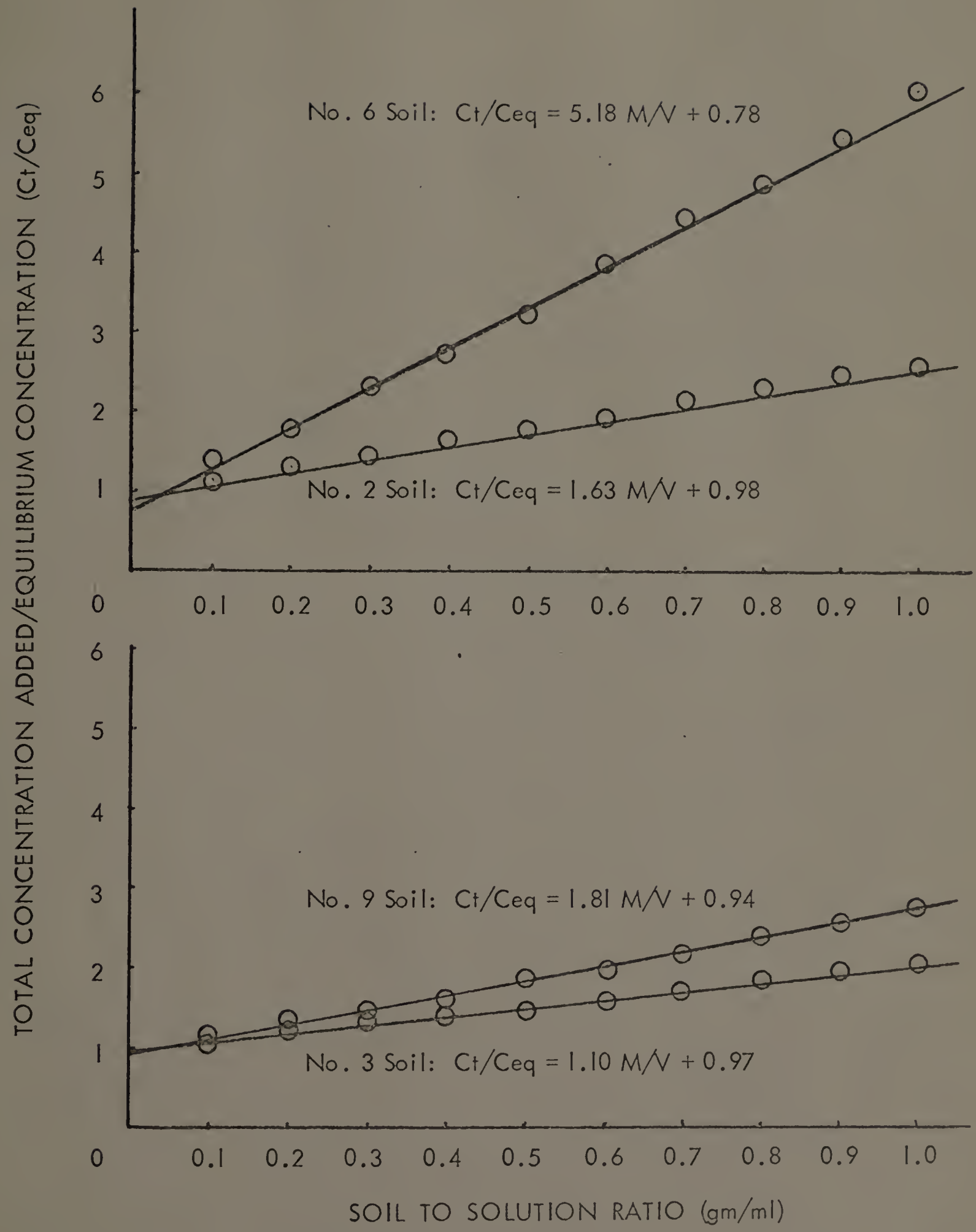

Figure 4. Plots for the effect of soil to solution ratio on the distribution coefficient (K_d) of atrazine for soil No. 2, No. 3, No. 6, and soil No. 9.

soil No. 6 exhibited relatively great deviation in the value of intercept from the theoretical value of 1. Nearpass (77) concluded that from his data, K_d was constant within the range of solution to soil ratios from 1 to 1 to 5. The increased total amount of atrazine available for soils to adsorb resulted in the increase in adsorption per unit weight of soil samples with widening the soil to solution ratio in his experiment as well as in this work.

The K_d values obtained from the adsorption isotherm and from the experiment of soil to solution ratio were in good agreement. The data from the soil to solution ratio experiment with soil No. 9 were combined with the adsorption isotherm data in a single graph and presented in Figure 7. The figure indicates that these two experiments are essentially the two sides of a coin with regard of the definition of K_d. This graph tells that at least up to 10 ppm atrazine in the equilibrium solution the K_d is constant. This concentration is much greater than the atrazine concentration to be expected in the soil solution in the field. Once the K_d of a soil is determined and the amount of atrazine which is to be applied to the soil is given, the amount of this herbicide which is to be adsorbed by the soil can be calculated with the known value of soil moisture content. It is obvious that the drier the soil condition, the greater will be the amount of atrazine adsorbed.

A direct application of the results obtained from this work may be found in the field. K_d may be expressed by equation (9);

$$K_d = \frac{fa}{(1 - fa)} \cdot \frac{(V)}{(M)} \qquad (9)$$

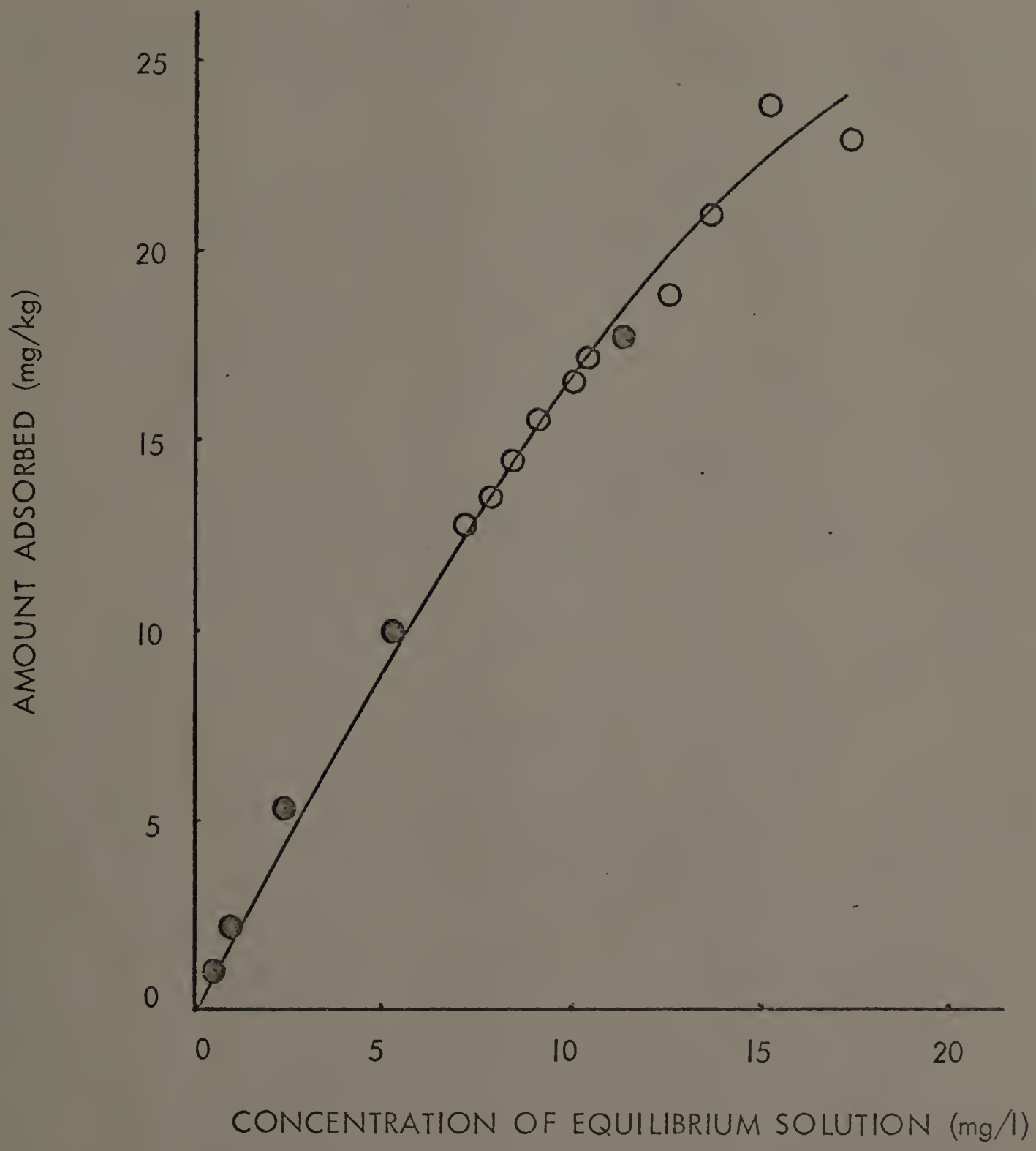

Figure 7. Combination of the data of the adsorption isotherm and the converted data of the experiment of soil to solution ratio.

where fa is the fraction of atrazine adsorbed by the soil and (1 - fa) the fraction of atrazine left in solution which is equal to fs, V is the volume of solution in ml, and M the weight of soil in gm. The equilibrium solution concentration is obtained by equation (10)

$$Ceq = \frac{A \quad fs}{V} = \frac{A \quad (1 - fa)}{V} \tag{10}$$

where A is the total amount of atrazine added to the soil expressed in μ gm. Equation (11) is derived from equations (9) and (10).

$$Ceq = \frac{A/M}{(V)/(M) \quad + \quad K_d} = \frac{(ppm) \quad added}{(V)/(M) \quad + \quad K_d} \tag{11}$$

where (ppm) added is the amount of atrazine added to the soil which may be expressed by either μg/g, mg/kg, or ppm. If it is assumed, in order to obtain the same herbicidal effect when atrazine is added to soils with different K_d values, that the concentration of atrazine in the soil solution should be the same, this equation (11) will give the amount of atrazine to be applied to the soils to provide same concentration of atrazine in the soil solutions. Usually the weight of an acre of a furrow soil layer is 2 million pounds by dry soil. Thus, if 2 lbs/A of atrazine, equivalent to 1 ppm of atrazine, is added to a series of soils and the moisture content (V/M) of the soils is 0.2, then at equilibrium the concentration of atrazine in soil solutions of soils with different K_d values are calculated to be 5 ppm for K_d value of 0, 0.83 ppm for K_d value of

1, 0.45 ppm for K_d value of 2, 0.24 ppm for K_d value of 4, and 0.12 ppm for K_d value of 8. If, for example, 0.5 ppm of atrazine in the soil solution is required to kill weeds, the amounts of atrazine that should be applied to soils to obtain 0.5 ppm of atrazine in the soil solution are 0.2 lbs/A to the soil with K_d value of 0, 1.2 lbs/A to the soil with K_d value of 1, 2.2 lbs/A to the soil with K_d value of 2, 4.2 lbs/A to the soil with K_d value of 4, and 8.2 lbs/A to the soil with K_d value of 8. Thus, an increase in K_d value by factor of 2 requires 2 times as much as atrazine for same herbicidal effect at 20% moisture content. A change of moisture content in a soil may not affect the concentration of atrazine in the soil solution very much. If a soil has K_d value of 4 and the soil solution should contain 0.5 ppm of atrazine for weed control, the amounts of atrazine to be applied to the soil are 4.6 lbs/A to 60% of soil moisture content, 4.4 lbs/A to 40% of soil moisture content, 4.2 lbs/A to 20% of soil moisture content and 4.1 lbs/A to 10% of soil moisture content. This calculation is contrary to the experiment of Grover (39) who found that increasing amounts of atrazine were required as soil moisture content decreased in order to obtain the same effect on the growth of oats. If the amount of atrazine in soil solution must be kept constant for the same herbicidal effect, and the soil has K_d value of 4, the amounts of atrazine which should be added to the soil are 1.54 lbs /A to the soil with 60% soil moisture content, 2.2 lbs/A to the soil with 40% soil moisture content, 4.2 lbs/A to the soil with 20% soil moisture content and 8.2 lbs/A to the soil with 10% soil moisture content. This agrees with the conclusion of Grover (39).

Uncertainties In The Results

Most of the preliminary studies were conducted with soil No. 9. The highest K_d value measured was 2.66, as shown in Table I in the Appendix. The lowest was 1.81, the slope of the regression line in Figure 4. The other 4 values were between these two extremes. Three of the total 6 values were very close to each other; 1.90, the average value obtained from the experiment of salt concentration and adsorption, 2.02, the average value in the adsorption isotherm, and 1.81, the slope of the regression line in Figure 4. Coefficient of variability (CV) was calculated using the 6 values of K_d, to be 15%. Eliminating the highest value, 2.66, yielded 11% for the CV. The three very close K_d values gave the CV the value of 5.5%.

V. SUMMARY

Experiments were conducted to study some aspects of the adsorption of atrazine by representative soils from Massachusetts. The following conclusions were extracted from this study:

1. Equilibrium in the adsorption of atrazine by soils was attained within a few hours.
2. Salt ($CaCl_2$) added to the soil solution did not affect the adsorption of atrazine at salt concentrations which are normally found in the field.
3. Adsorption of atrazine was very closely correlated with soil organic carbon content.
4. The distribution coefficient (K_d) of atrazine in a Massachusetts soil was varified to be constant regardless of both the concentration of atrazine in solution and of the soil to solution ratio.

VI. APPENDIX

TABLE I. PROPERTIES OF REPRESENTATIVE MASSACHUSETTS SOILS

Soil No.	pH 1:1 H_2O	pH 0.01M $CaCl_2$	Exchangeable cations (mc/100gm soil) H + Al	Al	Ca	Mg	K	Sum of cations	% Base Satu.	% Sand	% Silt	% Clay	% O-C	Atrazine K_d	Location (Mass.)
1	-	-	-	-	-	-	-	-	-	67.2	26.0	6.8	-	-	-
2	5.91	5.36	0.13	0.08	3.32	0.28	0.12	3.80	95	66.4	26.8	6.8	1.69	2.45	Belchertown
3	5.26	5.06	0.39	0.29	3.50	0.82	0.25	4.86	89	61.2	23.6	15.2	1.24	1.33	So. Deerfield
4	5.92	5.48	0.14	0.12	1.92	0.89	0.10	3.03	93	60.0	29.2	10.8	1.61	2.74	So. Deerfield
5	5.36	4.99	0.54	0.44	2.43	0.28	0.15	3.30	82	56.0	30.4	13.6	2.64	3.10	Belchertown
6	5.50	5.13	0.27	0.18	4.71	0.99	0.10	5.98	95	55.6	28.8	15.6	4.16	6.30	Belchertown
7	5.02	4.56	1.14	1.07	0.79	0.18	0.20	2.24	43	52.8	35.2	12.0	2.40	3.17	Belchertown
8	4.65	4.29	1.63	1.62	0.65	0.10	0.10	2.47	30	50.4	34.8	14.8	1.73	2.76	Amherst
9	5.02	4.83	0.57	0.48	2.19	0.42	0.24	3.33	78	50.4	34.4	15.2	2.37	2.59	Amherst
10	5.11	4.70	1.01	0.95	1.55	0.13	0.14	2.77	61	50.0	34.0	16.0	1.66	4.79	Belchertown
11	4.97	4.98	0.54	0.35	3.32	0.11	0.20	-	-	46.8	35.2	18.0	2.93	3.61	Amherst
12	5.25	5.05	0.27	0.18	4.27	0.97	0.19	5.61	93	46.0	38.4	15.6	3.00	8.29	Belchertown
13	5.51	5.15	0.36	0.27	2.01	0.59	0.11	2.98	87	44.8	41.6	13.6	1.46	1.92	Belchertown
14	-	-	-	-	-	-	-	-	-	32.4	57.2	10.4	-	-	-
15	5.71	5.54	0.15	0.13	3.20	0.74	0.22	4.29	92	30.0	56.8	13.2	1.18	1.30	So. Deerfield
16	6.49	6.40	0.04	0.00	10.75	5.02	1.30	17.07	100	28.8	26.8	44.4	2.88	1.82	Amherst
Av.	5.41	5.11	0.51	0.44	3.19	0.82	0.24	4.75	80	49.9	34.0	16.1	2.37	3.30	

VI. APPENDIX

TABLE II. PROPERTIES OF SIX SOIL PROFILES OF MASSACHUSETTS

Soil	Horizon	Depth (inches)	pH 1:1 H_2O	pH 0.01M $CaCl_2$	% O-C	K_d	Location (Mass.)
Agawam	Ap	0 - 9	4.90	4.42	1.28	1.24	Hadley
fine sandy	B21	9 - 17	4.61	4.50	0.25	0.02	
loam	C1	17 - 36	4.71	4.70	0.10	0.13	
(Cultivated)	C2	36 - 46	4.75	4.72	0.08	0.14	
Berkshire	Ap	0 - 9	4.76	4.48	4.00	5.80	Hawley
loam	A2	9	-	-	0.26	3.09	
(Cultivated)	B21	10 - 14	-	-	-	-	
	B22	14 - 18	-	-	-	-	
	B3	18 - 27	5.11	4.68	1.61	0.54	
	C1	27 - 38	5.02	4.70	0.84	0.45	
	C2	38 - 46	4.87	4.75	0.22	0.18	
Charlton	A00	2 - 1	-	-	-	-	Sutton
stony fine	A0	1 - 0	-	-	-	-	
sandy loam	A1	0 - 1	-	-	-	-	
(Forested)	B21H	1 - 4	4.10	3.82	4.61	8.29	
	B22	4 - 10	4.30	4.08	1.11	2.98	
	B23	10 - 23	4.55	4.49	0.52	1.51	
	B24	23 - 33	4.42	4.76	0.35	0.14	
	C	33 - 39	4.78	4.88	0.20	0.02	
Essex	Ap	0 - 8	5.59	5.21	-	-	Plymouth
fine sandy	B21	8 - 13	5.25	4.69	0.80	0.58	
loam	B22	13 - 19	4.91	4.46	0.62	0.57	
(Cultivated)	B23	19 - 26	4.82	4.51	0.41	0.45	
	Clgm	26 - 37	5.09	4.64	0.28	0.05	
Hadley	Ap	0 - 12	5.31	4.76	0.97	0.39	Northampton
very fine	C1	12 - 20	5.56	5.05	0.58	0.08	
sandy loam	C2	20 - 27	5.62	5.10	0.46	0.09	
(Cultivated	A1b	27 - 30	5.65	5.10	0.71	0.21	
	C2b	30 - 38	5.64	5.10	0.43	0.10	
	A2b	38 - 45	5.68	5.09	0.71	0.15	
	C3b	45 - 57	5.41	5.02	0.35	0.37	
Paxton	Ap	0 - 9	-	-	-	-	New
fine sandy	B21	9 - 16	4.52	4.16	0.95	1.30	Braintree
loam	B22	16 - 27	4.51	4.05	0.39	1.59	
(Forested)	Cm	27 - 35	4.70	4.06	0.25	1.04	

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ADSORPTION OF ATRAZINE
ON REPRESENTATIVE MASSACHUSETTS SOILS

A Thesis

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